I. THE PREPARATION AND POLYMERIZATION OF SOME SUBSTITUTED STYRENES

II. THE TOTAL STRUCTURE OF COPOLYMERS OF BUTADIENE AND STYRENE BASED ON OXIDATION EXPERIMENTS

BY

JOHN DAVIS YOUNG

B.S., University of North Carolina, 1943

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
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PART I

THE PREPARATION AND POLYMERIZATION OF SOME SUBSTITUTED STYRENES

Introduction

The low supply of natural rubber in the United States during the war necessitated the production of large amounts of some synthetic rubber for use in all types of vehicle tires. The synthetic rubber produced in greatest amounts for this purpose, GR-S, is inferior to natural rubber in some properties. A continuous effort has been made to attempt to correct these defects and to develop new synthetic elastomers which might have properties more closely approximating those of natural rubber. One approach to this problem has been the determination of the effect of replacing one of the comonomers in GR-S, styrene, with certain substituted styrenes. In a continuation of this program five substituted styrenes, 3,5-dichlorostyrene, 3-phenylstyrene, 4-methylstyrene, 4-isopropylstyrene, and 4-*tert.*-butylstyrene have been prepared and copolymerized with butadiene in quantities sufficient to permit a laboratory evaluation of the copolymers. The polymers of these compounds have also been prepared and characterized.

Discussion of Results

3,5-Dichlorostyrene has been prepared from 3,5-dichlorobenzaldehyde which was synthesized from *o*-toluidine according to a modification of the procedures of Asinger and Lock[1] and Lock and Bock.[2] This aldehyde was converted to 3,5-dichlorophenylmethylcarbinol by treatment with methyl magnesium iodide, and this carbinol was dehydrated over fused potassium acid sulfate by the method of Marvel and Schertz[3] to give 3,5-dichlorostyrene.

3-Phenylstyrene was made from 3-bromobiphenyl which was prepared according to the method of Huber and co-workers.[4] This 3-bromobiphenyl was converted to the Grignard reagent which was treated with acetaldehyde to give 3-phenylphenylmethylcarbinol. Dehydration of this carbinol by the procedure of Mowry, Renoll, and Huber[5] gave 3-phenylstyrene.

4-Isopropylstyrene and 4-*tert.*-butylstyrene were prepared from isopropylbenzene and *tert.*-butylbenzene, respectively. Acetylation by the method of Perrier[6] as used by Mowry, Renoll, and Huber[5] gave the corresponding *para*-substituted acetophenones. Reduction of the ketones to the carbinols with aluminum isopropoxide was accomplished using a modification of the procedure of Lund.[7] Dehydration of 4-isopropylphenylmethylcarbinol to form the styrene was accomplished by the method used for 3,5-dichlorostyrene. 4-*tert.*-Butylphenylmethylcarbinol was converted to 4-*tert.*-butylstyrene by the same procedure used for the preparation of 3-phenylstyrene.

4-Methylstyrene was prepared from *p*-tolyl methyl ketone. Reduction of this ketone with Raney nickel gave 4-tolylmethylcarbinol which was subsequently dehydrated by the procedure used for 3-phenylstyrene to give 4-methylstyrene.

A polymer of each of the substituted sytrenes was made by exposing the monomer to ultraviolet light. Copolymers of each of the monomers were made by emulsion copolymerization with butadiene. Industrial evaluation indicated that on the whole the copolymer of 3,5-dichlorostyrene was little better than ordinary butadiene-styrene copolymers.[8] The remainder of the copolymers have been submitted for evaluation.

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PART II

THE TOTAL STRUCTURE OF COPOLYMERS OF BUTADIENE AND STYRENE BASED ON OXIDATION EXPERIMENTS

Introduction

In view of the heterogeneity of the GR-S molecule much attention has been given to the determination of the exact structure of the butadiene-styrene copolymer. The main approach to this problem has been an oxidative scission of the rubber molecule at the double bonds followed by an isolation and identification of the products. However, certain fragments thus obtained, particularly those containing phenyl groups, have remained unidentified. In a continuation of this work, a preliminary examination has been made of the products obtained by the oxidation of GR-S by means of *tert.*-butyl hydroperoxide and osmium tetroxide. The purpose of this investigation has been primarily to determine the worth of this oxidation method as a tool for structure determination work.

Discussion of Results

It has been found by Laitinen and coworkers[1] in this laboratory that GR-S could be cleaved with the production of carboxylic acids by means of *tert.*-butyl hydroperoxide in the presence of osmium tetroxide. However, in benzene solution only 60-70 per cent of the theoretical quantity of acids (based on the oxidation of each double bond to carboxylic acids) could be obtained. In a two-phase, alkaline oxidation system, greater quantities of acids could be obtained, but blank experiments showed that under these conditions acids could be produced by an oxidation of the solvent system. Whether in the alkaline oxidation the increased yield of carboxylic acids was due to a further oxidation of GR-S or an oxidation of the solvent is not known.

In the present investigation, which was carried out in cooperation with Laitinen and coworkers, the carboxylic acids obtained from GR-S by this oxidation method were converted to their methyl esters by treatment with methanolic hydrogen chloride or according to the method of Weissberger and Kilber.[2] In each esterification experiment, it was found that approximately 25 per cent of the methyl esters obtained were insoluble in ether. This insolubility of the esters in ether indicated that some of the products obtained by this oxidation method were unlike those resulting from the degradation of GR-S by the ozonolysis method, for Rabjohn and coworkers[3] reported that the esters obtained in their work were completely ether-soluble.

The presence of an appreciable quantity of 1,2-glycol-containing substances in the degraded polymer solution has been shown by periodic acid oxidation experiments. This evidence indicated that some of the 1,2-glycols produced by a hydroxylation of the double bonds of the oxidizing agent were not being cleaved to produce carboxylic acids. Other evidence has also been obtained to indicate the presence of hydroxyl groups in the material in the degraded polymer solution, particularly in the ether-insoluble portion of esters.

These hydroxyl groups may have been a contributing factor to the ether-insolubility of the esters.

The oxidative cleavage of GR-S by means of *tert.*-butyl hydroperoxide and osmium tetroxide as used did not appear to be an entirely satisfactory method for degradation of GR-S for structure determinations, since a quantitative yield of carboxylic acids derived from a scission of the ethylenic linkages was not obtained.

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VITA

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